Topics in Current Chemistry

90

M. Venugopalan, U. K. Roychowdhury,
K. Chan, and M. L. Pool
Plasma Chemistry
of Fossil Fuels

M. Capitelli and E. Molinari
Kinetics of Dissociation Processes
in Plasmas in the Low
and Intermediate Pressure Range

Plasma Chemistry II

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Plasma Chemistry of Fossil Fuels

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1 Introduction

Fossil fuels are the subterranean remains of green plants and animals that once grew and then were buried in sedimentary sands, muds and limes under conditions of incomplete oxidation. The present supply of fossil fuels includes coal, oil, natural gas, oil shale and tar sands. Natural gas is the fossil fuel in shortest supply and greatest demand. The simple hydrocarbon methane is the predominant component and represents 80–95 volume percent of any natural gas. Over the years several techniques have been applied to produce methane from other fossil fuels such as petroleum which is a mixture of hydrocarbons with six or more carbon atoms and coal which is a complex mixture of some organic compounds. One such technique is the production of a plasma in petroleum and coal through the action of either very high temperatures or strong electric fields. Since coal is in greatest supply the objective included obtaining new knowledge of coal chemistry, which may lead to new methods of producing organic chemicals.

The properties of the plasma produced in fossil fuels vary widely. Those plasmas labeled "glow discharges" are characterized by average electron energies of 1–10 eV, electron densities of 10^{15}–10^{18} m^{-3} and lack thermal equilibrium in the sense that electron temperatures are much greater than gas kinetic temperature ($T_e/T_g = 10$–100). The absence of thermal equilibrium makes it possible to obtain a plasma in which the gas temperature may have near ambient values while at the same time the electrons are sufficiently energetic to cause the rupture of molecular bonds. It is this characteristic which makes glow discharges well suited for the study of chemical reactions involving thermally sensitive materials such as petroleum and natural gas. By contrast, plasmas labeled "arcs" or "jets" have nearly identical electron and gas temperatures (> 5000 K). The high gas temperature makes these plasmas suitable for producing chemicals by degrading complex organic materials such as coal, shale and tar. The highly excited species that exist in these plasmas can react to produce compounds whose formation is thermodynamically unfavorable under ordinary experimental conditions. The physical and chemical properties and the production of both types of plasmas have been fully described elsewhere1).

Because of the complex structure of coal and the variable composition of petroleum most of the plasma work using these materials is descriptive in nature. Attempts at modeling have been confined to the carbon-hydrogen system, chiefly using graphite, perhaps due to its importance in nuclear fusion and as aerospace material. In this chapter the studies of coal, petroleum hydrocarbons and natural gas in glow discharges, electrical arcs and jets are reviewed. Also reviewed are those studies in which these fossil fuel plasmas are formed in presence of simple gases such as hydrogen, nitrogen and argon. A comparison is then made with those studies in which lasers and flash heating techniques were applied. Pertinent investigations on the structural aspects of plasma-treated coal are included. Finally, the status of work on plasma desulfurization and gasification of coal and petroleum is discussed.

2 Thermodynamic and Kinetic Aspects of Fossil Fuel Chemistry

Thermodynamic considerations of the carbon-hydrogen system provide a useful guide to the nature and yield of products which might be obtained from fossil fuels at the temperatures attained in various plasma devices.

At temperatures between 900 and 2000 K most hydrocarbons have a positive free energy of formation, which, with the exception of acetylene, increases with increasing temperature$^{2)}$. Below 500 K only the paraffinic hydrocarbons are thermodynamically stable. Above 1700 K acetylene has a lower free energy of formation than the other hydrocarbons, but it is still thermodynamically unstable. Consequently, acetylene can be obtained by rapidly carbonizing fossil fuels at about 1800 K, but the yield is still mainly governed by chemical kinetics$^{3)}$. That is to say, the reaction time must be sufficiently long to permit the decomposition of other hydrocarbons to acetylene, but sufficiently short to prevent any appreciable decomposition of the acetylene formed to carbon and hydrogen. At temperatures of about 4000 K, the free energy of formation of acetylene from its elements approaches zero, and the equilibrium yield of acetylene is appreciable. The system is complicated, however, by other reactions and phase changes which occur at these high temperatures. For example, carbon sublimes at about 4000 K, molecular hydrogen dissociates, and various species such as C, C_2 and C_3 are formed.

Coals, particularly the bituminous and sub-bituminous varieties, undergo primary decomposition in the temperature range of 700–800 K. If coal carbonization could attain thermodynamic equilibrium over this temperature range, the hydrocarbon products with the exception of methane, if any, would be decomposed mainly to carbon and hydrogen. In practice, thermodynamic equilibrium is not attained, and the composition of the hydrocarbon by-products is mainly determined by the temperature and the kinetics of the process.

The equilibrium between carbon and hydrogen at high temperatures has been treated thermodynamically by several authors$^{4,5)}$. The approach was to formulate the various reactions which could possibly occur, to apply to each the appropriate mass action equation, and to solve the set of simultaneous equations so obtained. A distinction was made between heterogeneous and homogeneous systems, since for the latter it is necessary to specify the mole ratio of carbon to hydrogen (C/H) in the system.

Assuming that the equilibrium composition of a reaction mixture with C/H = 1.0 at 2000–5000 K would consist of C, C_2, C_3, C_s, H, H_2, CH, C_2H, C_3H, C_4H, CH_2, C_2H_2 and C_4H_2, Baddour and Blanchet$^{5)}$ found that the mole fraction of acetylene in the equilibrium mixture passes through a maximum with temperature, the value being 0.07 at 3300 K while that of C_2H is 0.1 at 3800 K. To apply this information to the products obtained at room temperature they assumed that C_2H_2 remained unchanged on quenching, while C_2H recombined with H to yield more C_2H_2. On this basis, the theoretical maximum acetylene concentration in the quenched gas was found to depend on the temperature and C/H ratio of the system: At 3200 K, with a C/H ratio of 0.25 (as for CH_4) the maximum volume percentage of acetylene in the quenched gas is 12; with a C/H ratio of 0.50, the amount of acetylene can be increased to 19%.

At 4300 K and a C/H ratio of 15, the maximum concentration is 50%, a value considerably higher than those found in experiments using high intensity arc reactors.

The kinetic aspect of the reaction between graphite and hydrogen has been studied[6)]. At temperatures above 3000 K, the sublimation of graphite is the controlling factor, and the reaction rate is independent of hydrogen pressure provided that there are sufficient hydrogen molecules to react with all the C_n species that evaporate. Below 3000 K, the reaction of graphite and hydrogen between 0.01 and 1 atm is a surface reaction whose rate is proportional to the hydrogen pressure and the square root of the dissociation constant of hydrogen. Several authors have investigated the reaction of graphite in low pressure discharges at relatively low temperature of hydrogen. Veprek and coworkers[7)] have shown that both the diffusion of H atoms towards the carbon surface and the diffusion of reaction products from the surface are much faster than the rate of surface recombination and the surface reaction. For pyrolytical graphite the probability of the reaction defined as the ratio of the number of C atoms leaving the surface to the number of H atoms impinging on the surface is about 10^{-4} or less. Since the reaction probability would depend strongly on the quality of the carbon used, it would be much higher for carbon of a poor quality, such as that found in coal.

Under plasma conditions any oxygen present in the coal will be evolved as carbon monoxide. If the carbonization is carried out in nitrogen atmosphere, acetylene and hydrogen cyanide will be the main products. Very little cyanogen would be formed unless the nitrogen is greatly in excess of the hydrogen in coal[8)]. For a discussion of the thermodynamics of the C–H–N system the reader is referred to an article by Timmins and Ammann[9)]. The chemical evaporation, transportation and deposition of carbon in low pressure discharges of oxygen, nitrogen and hydrogen have been described recently[10)].

3 Natural Gas and Methane Plasmas

Natural gas as obtained from underground deposits generally has a composition that is significantly different from that of the familiar commercial fuel. The crude gas usually contains some undesirable impurities such as water vapor, hydrogen sulfides, and thiols or other organic sulfur compounds in addition to some heavy, condensable hydrocarbons[11)]. Appropriate processing eliminates or reduces the amount of the undesirable impurities and allows the condensable hydrocarbons to be collected as a separate fraction of industrial value. The following volume composition for the commercial fuel is thus arrived[12)]: 80–95% CH_4, 8–2% C_2H_6, 3–1% C_3H_8, < 1% C_4H_{10}, < 1% C_5H_{12}, 10–0% N_2, <2% CO_2. The concentrations of the minor components vary slightly with the source of the gas.

3.1 Low Frequency Discharges

The decomposition of methane in the glow discharge has been investigated for many years. At low pressures ethane was the major product[13)]. As the methane pressure was increased, ethylene and acetylene were formed; their concentrations in the product became significant if the reactor was cooled in liquid air[14–16]. In a flow system at atmospheric pressure under conditions of high conversion and relatively high temperatures Wiener and Burton[17] found that the yield of acetylene was quite high.

In the negative glow[18] of a dc discharge in methane at low pressures (0.05–0.3 torr) and low currents (0.1–5 mA) ethane, ethylene and acetylene were found in addition to hydrogen and the nonvolatile cuprene, $(CH)_n$, which appeared mainly on the cathode as a solid. Lowering the temperature of the reactor from 77 K to 63 K greatly increased the amount of ethylene. Smaller amounts of propane, propene, propyne, butane, butene, butadiene and pentene were also found. Their rates of formation increased with increasing discharge current at the expense of the C_2 hydrocarbon products and cuprene. The addition of hydrogen to the methane had little effect on the products. Variation of the inter-electrode separation indicated that the products were not formed uniformly throughout the negative glow.

Recently a movable glow discharge of methane has been investigated mass spectrometrically over the whole column length[19]. The mass spectra showed primary fragment ion of methane and ions from condensation reactions up to m/e = 113. The current of different ions reached a maximum very close to the cathode and varied regularly along the axis in maximum and minimum which were related directly with the striations of the column. By simulating the conditions of the glow discharge in a mass spectrometer with high pressure ion source the same ion-molecule reactions were identified with which it was possible to explain the formation of condensation-type ions in the discharge.

Methane has been decomposed in ac discharges operated using 1–6 kV and 30–70 mA in flow systems at pressures of 1–10 torr[20]. With contact times of 0.05–1.5 s the principal products were acetylene, ethane, ethylene and hydrogen together with some higher molecular weight compounds. The conversions which varied from 28 to 91% increased on increasing the contact time and/or discharge current. However, the yields of C_2 and C_3 hydrocarbons reached a maximum at 40–50% total conversion. Almost complete conversions of methane to acetylene have been reported in later works[21, 22]. Vishnevetskii et al.[23–25] have given a set of equations for calculating the rates of acetylene and ethylene formation and the rates of decomposition of several hydrocarbons.

Several attempts[26–31] have been made to analyze the numerous higher molecular weight products from line frequency spark and pulsed discharges in methane at pressures of 250–500 torr. The work is of great interest in connection with the chemistry of primitive earth atmosphere and the origin of life.

The kinetics of conversion of methane to acetylene in glow discharges has been studied in detail[32–35]. A great amount of this work has centered around such parameters as power yields, pressure, cell design, electrode material and presence of hydrogen or argon. Methane conversion was hindered by H_2 or Ar to the same extent and was greater with greater partial pressure of these added gases in the pressure range 40–150 torr. However, the cracking of methane was accelerated by H_2 and Ar at a total pressure of 10 torr. Compared with the higher paraffins, methane yielded the least amount of acetylene. The cracking rate constant increased with pressure. With increasing specific power (power per unit volume of input methane) consumption the degree of conversion increased gradually on inactive and little carbonized, but rapidly on active and carbonized electrodes.

Glow discharges at low pressures in mixtures of methane and nitrogen produced acetylene simultaneously with hydrogen cyanide36). C_2H_2/HCN ratios varied according to the current densities and mixture compositions used. When mixtures of methane and carbon dioxide or methane and water were subjected to discharge, carbon monoxide and hydrogen were produced. Acetylene was found only at low current densities37).

The production of acetylene from natural gas has been studied in a 60 Hz electrical discharge at atmospheric pressure38). The apparatus consisted of a cyclone-type reactor in which the products could be removed through a hollow electrode. The electrode separation was 2 cm; the potential difference necessary for spark over gas was 13–16 kV. By varying the residence time of the gas in the reactor from 30 to 600 s a product containing 15–17% C_2H_2 by volume was obtained at relatively low temperatures. Increasing the input rate and decreasing the specific power consumption increased the amount of C_2H_2 formed, but decreased the C_2H_2 concentration in the product. Copper electrodes were reported to produce the least deposition of carbon black and cuprene.

3.2 Triboelectric Discharges

Methane has been converted into ethane, ethylene, acetylene and hydrogen in a "triboelectric" discharge arising from the intermittent contacting of mercury with a glass surface39, 40). The discharge is a result of the accumulation of high densities of static charge at the interface by the transfer of electrons from the mercury to the glass. Spectroscopic studies of the discharge have indicated that excited species with energies up to 20 eV above their ground states are present. Further, the triboluminescence spectrum differed from the spark discharge spectrum at atmospheric pressure in that C_2 emission was absent. Both area and nature of the solid surface influenced the extent of breakdown and discharge. The rates of methane conversion were virtually invariant with pressure from 760 to 200 torr, but at 200 torr they increased sharply before gradually falling off again as the pressure was further reduced. The addition of 10% noble gases did not result in any pronounced change in the C_2 hydrocarbon yields or affect the product distribution which was $C_2H_6:C_2H_4:C_2H_2 = 1:0.34:0.32$.

3.3 High Frequency Discharges

Eremin41) reported that the amount of methane cracked by a high frequency discharge is proportional to the current consumed and to the amount of excess hydrocarbons. The reaction was found to be of the first order and the rate was directly proportional to the discharge energy and inversely proportional to the original amount of methane. The amount of methane reacting per unit energy consumed was practically independent of the shape of the discharge, the current density and the methane dilution with hydrogen and was lower at higher pressure.

The decomposition of methane has been studied in a 2.45 GHz glow discharge sustained by microwave fields42). With 150–310 V/cm, methane pressures in the range 16–220 torr and residence times in the range 0.01–10 s acetylene was the principal product, the maximum yield attained being 31 g $kWhr^{-1}$. Ethane and ethylene were produced in significant amounts from methane only when the effluent discharge gas was allowed to impinge directly on a liquid-nitrogen-cooled wall. If only stable molecules had been formed in the plasma, the cold wall would not have altered the products. This was taken as evidence that free radicals do not recombine instantly but persist as such for some time after leaving the plasma zone.

Vastola and Wightman43, 44) found an increase in H_2^+ and a decrease in CH_3^+ when methane was passed through a 2.45 GHz microwave discharge at 0.15 torr and 40 W. With a ten-fold increase in power Baddour and co-workers45) could efficiently produce carbon black and hydrogen from methane.

Radiofrequency (1–200 MHz) discharges in methane have been studied. Miquel and Chirol46) observed that the decomposition followed a first-order rate law. Le Goff et al.47) found that ethane and acetylene constituted 80% of the products. In a recent study Simionescu et al.48) identified H_2, C_2H_6, C_2H_4 and C_2H_2 among the products of methane decomposition by *in-situ* gas chromatographic analysis. Their ratio was found to depend on the time and power of the rf discharge (Fig. 1). In one investigation49) products such as ethylacetylene, cyclopentadiene, indene and formaldehyde have also been reported. The formation of formaldehyde appeared to indicate the presence of oxygen or water in the methane sample50).

Studniarz and Franklin51) have studied the relative ionic composition of a 50 MHz plasma in methane. Using a quadrupole mass spectrometer and a fast-flow low power discharge they detected CH_3^+, CH_4^+, CH_5^+ and $C_2H_5^+$, in varying proportions depending on pressure, in the range 0.02–0.4 torr. In this work the discharge conditions were chosen so as to minimize polymer formation.

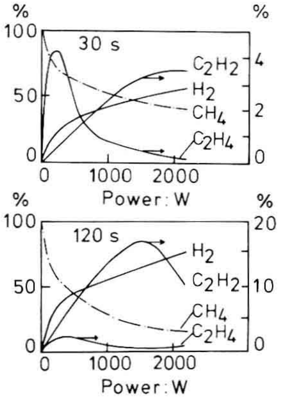

Fig. 1. Power dependence of the decomposition of methane (*broken curve*) and the product yields at 30 s and 120 s discharge periods. (Redrawn from Simionescu, Cr.I., Dumitriu, S., Bulacovschi, V., Onac, D.: Z. Naturforsch. *30b*, 516 (1975), by permission of the publishers, Verlag der Zeitschrift für Naturforschung)

Table 1. Ionic, radical and neutral species observed in an rf plasma in methane[52)]

Ions				Radicals	Neutrals	
Major (I > 5%)		Minor (I < 5%)			Major	Minor
High pressure	Low pressure	High pressure	Low pressure			
$C_2H_3^+$	CH_3^+	CH_3^+	H_2^+	$CH_2^\cdot$	H_2	C_3H_4
$C_2H_5^+$	CH_4^+	CH_5^+	H_3^+	$CH_3^\cdot$	C_2H_2	C_3H_8
$C_3H_3^+$	CH_5^+	$C_2H_2^+$	$C_2H_2^+$	$C_2H_3^\cdot$	C_2H_4	
$C_3H_5^+$	$C_2H_3^+$	$C_2H_4^+$	$C_2H_6^+$	$C_2H_5^\cdot$	C_2H_6	
$C_3H_7^+$	$C_2H_4^+$	$C_2H_6^+$	$C_3H_3^+$	$C_3H_7^\cdot$		
	$C_2H_6^+$		$C_3H_7^+$			

With a relatively slow-flow and a 13.56 MHz discharge in methane Smolinsky and Vasile[52)] monitored the ionic and neutral products at pressures from 0.1 to 1 torr. Their data are summarized in Table 1. The neutrals were measured by adjusting the potentials on the focusing lenses so as to prevent all ions formed in the discharge from reaching the mass filter. Molecular hydrogen was the dominant product, its mole fraction as well as that of acetylene decreased steadily as the pressure was increased, while those of ethane and ethylene exhibited maxima in the pressure range 0.2–0.6 torr. C_3 hydrocarbons were an order of magnitude smaller than the C_2 hydrocarbons and the higher homologues were proportionately less. C_1 ions (CH_3^+, CH_4^+) and $C_2H_2^+$ decreased monotonically with increasing pressure, perhaps due to reduced electron energy. The change in intensity with increasing pressure of ions such as $C_2H_3^+$, $C_2H_5^+$, $C_3H_3^+$, $C_3H_5^+$ and $C_3H_7^+$ suggested that ion-molecule reactions were occurring in the system. Major differences were found in the observed products when these were sampled axially rather than radially.

Figure 2 shows the different sampling configurations used by Vasile and Smolinsky[53)]. Table 2 summarizes the mole fractions of the principal neutral products from

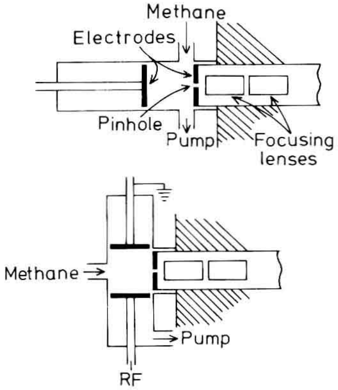

Fig. 2. Schematic representation of the axial (*upper*) and radial (*lower*) sampling configurations of a methane rf plasma for mass spectrometric analysis. (Redrawn from Vasile, M. J., Smolinsky, G.: Int. J. Mass Spectrom. Ion Phys. *18,* 179 (1975), by permission of the authors and the publishers, Elsevier Publishing Company)

Table 2. Mole fractions of neutral products from a 0.45 torr 150 V methane rf plasma[53)]

Product	Sampling mode Axial sampling through the rf electrode	Axial sampling through the ground electrode	Radial sampling through an electrically floating orifice
H_2	0.31	0.23	0.15
CH_4	0.60	0.70	0.78
C_2H_2	0.019	0.013	0.012
C_2H_4	0.013	0.011	0.011
C_2H_6	0.055	0.041	0.045

a 0.45 torr 150 V discharge. Axial sampling through an internal rf capacitor electrode yielded C^+, CH^+, CH_2^+, CH_3^+, $C_2H_2^+$ and $C_2H_3^+$ as the dominant ions, with very little abundance of ions containing greater than three carbon atoms. Radial sampling of a capacitively coupled discharge showed CH_3^+, CH_5^+, $C_2H_3^+$ and $C_2H_5^+$ as dominant with a significant fraction of the total comprising C_4 to C_6 ions. The relative abundances of the C_2-ions are compared in Table 3. The dissimilarity is attributed to the difference in energy of the electrons which cause the ionization and the difference in kinetic energy of the ions that undergo ion-molecular reactions to yield secondary ions.

Investigations[54, 55)] of the cracking of natural gas (96% CH_4) by an electrodeless high frequency discharge have been reported. The products were H_2, C_2H_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8. An increase in the total gas conversion was observed with increasing temperature in the range 220–550 K and contact time in the range 0.04–2.4 s. Addition of H_2 (up to 50% of the total CH_4) caused a decrease, while addition of Ar (up to 75% of the total CH_4) resulted in an increase in the cracking of methane. The effects of the introduction of a number of solid catalysts into the plasma zone have also been reported[55)].

Table 3. Relative abundances of C_2-ions produced in a 0.45 torr, 150 V methane rf plasma[53)]

Ion	Sampling mode Axial sampling through the rf electrode	Radial sampling through an electrically floating orifice
$C_2H_2^+$	0.092	0.014
$C_2H_3^+$	1.0	0.46
$C_2H_4^+$	0.066	0.137
$C_2H_5^+$	0.36	1.0
$C_2H_6^+$	0.013	0.029

3.4 Electrical Arcs and Plasma Jets

When the current density of a luminous discharge exceeds a certain limit, the potential difference between the electrodes diminishes and the discharge becomes an arc. The arc is characterized by the low potential difference of tens of volts between the electrodes and the high current density which may reach several thousand amperes per square centimeter on the electrodes. When an arc is established between two electrodes in a stream of rapidly flowing gas, the plasma is pushed in the direction of flow. If the arc is formed in a chamber with a proper exit nozzle, a plasma jet is produced outside the chamber with electrons and ions present, in the complete absence of an external electric field.

Following the invention of the high intensity electric arc several attempts have been made to convert methane and natural gas to acetylene. Unlike solids, gaseous reactants induce instability in the arc column by appreciable forced convection⁵⁶⁾. For this reason several arc stabilization techniques were developed. These techniques⁵⁷⁾ include confinement of the arc column in a watercooled channel, vortex stabilization, magnetic stabilization, mixing the gaseous reactants with the arc effluent and/or injecting the gases through a specially designed annular nozzle surrounding an electrode.

In their early work Leutner and Stokes⁵⁸⁾ used methane-argon mixtures (1:4) in a plasma jet unsuccessfully. These mixtures melted the tungsten cathode instantaneously. In later experiments methane was introduced into the flame of an argon plasma jet. This was accomplished with the apparatus shown in Fig. 3 in which methane was introduced through a water-cooled annulus in the anode normal to the argon jet. About 80% by wt of the methane was converted to acetylene at temperatures estimated to be 1.2×10^4 K. Subsequently Anderson and Case⁵⁹⁾ applied thermodynamic and kinetic data to predict the results which could be obtained when methane was introduced into a hydrogen plasma jet and the mixture quenched. The agreement between their analytical treatment and experimental data is very good.

Because of the very high conversion of methane to acetylene the plasma jet process has received more attention than the pyrolytic process. A number of patents describing plasma jet processes of preparing acetylene from methane and higher paraffins have been registered⁶⁰⁻⁶⁶⁾. The reported energy consumptions vary from 7 to 11 kWhr kg^{-1} C_2H_2. The process is considered to be more efficient than the carbide process for manufacturing acetylene⁶⁷⁾.

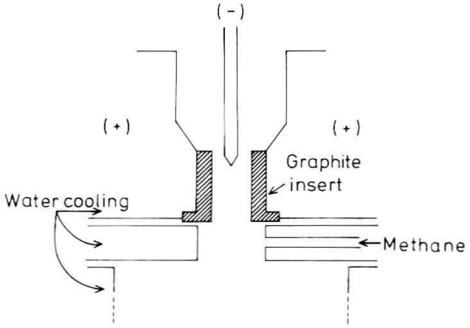

Fig. 3. Argon plasma jet with water-cooled annulus for methane pyrolysis. (Redrawn from Leutner, H. W., Stokes, C. S.: Ind. Eng. Chem. *53*, 341 (1961), by permission of the authors and the publishers, the American Chemical Society)

Eremin and coworkers[68–70)] using a high-tension ac arc found that a lower pressure in the 70–800 torr range greatly increased the methane conversion and acetylene production. The power efficiency could be doubled when the pressure was reduced to 70–10 torr. The addition of up to 37% by vol of hydrogen did not affect the acetylene concentration in the reaction products nor the power consumption which was 0.184 m^3 $kWhr^{-1}$. A somewhat lower C_2H_2 yield with a correspondingly higher power consumption was found only with mixtures which contained 48.4% H_2. In pilot-plant experiments the best results were obtained with an initial gas pressure of 42–46 torr natural gas when the power consumption was 3 kWhr m^{-3}. Sixty percent of the methane was cracked and 52% methane cracked with C_2H_2 production. The concentration of C_2H_2 in the product gas was 15%. Current strength and the electrode separation did not affect the proportion of CH_4 cracked or the total power consumption. These results confirmed calculations which were made on the asssumption of a first order reaction in the plasma and which took into account the concurrent reactions $2CH_4 = C_2H_2 + 3H_2$, $2CH_4 = C_2H_4 + 2H_2$ and $CH_4 = C + 2H_2$.

Il'in and Eremin[71–73)] reported that the cracking rate in an electrical arc is the same for several paraffins at 1.5 atm pressure and is a function of the energy supplied to the arc. While the maximum concentration of C_2H_2 in the products increased as the molecular weight of the cracking hydrocarbon increased, the energy consumption and heat effects decreased. In each case the degree of overall conversion followed a first order rate law. Preheating the methane to an adequate temperature, for example, 1000 K, increased the yield of C_2H_2 per unit energy input. Decreasing the length of the anode channel did not affect the process significantly but increasing its cross section increased the energy consumption and lowered the volume concentration of acetylene. The addition of $C_3H_8-C_4H_{10}$ to CH_4 increased the conversion of CH_4 to C_2H_2, the increase being a maximum for 2.5–4 vol % of the additives. It is known that higher hydrocarbons such as propane and butane give good yields of acetylene with less expenditure of energy[74–77)]. In a coaxial arc reactor at a specific energy consumption of 3.3 kWhr m^{-3} natural gas conversion into acetylene reached a maximum of 70%.

The effects of preheating natural gas before injection into the plasma jet have been studied by many workers. Whereas Il'in and Eremin[71)] observed that preheating at 600 K did not affect the results, Okabayasi et al.[78)] found an increase in acetylene yield per unit energy input. However, in agreement with Il'in and Eremin's observation at higher preheating temperatures, Kobozev and Khudyakov[79)] reported an increase in C_2H_2 concentration in the products from natural gas preheated to 800 K before injecting it into a 2800 K plasma jet.

In a series of papers and books published over a period of nearly two decades Polak has reported the work of his group at the Petrochemical Research Institute of the U.S.S.R. Academy of Sciences, Moscow[80–88)]. An electrode plasmatron was used which operated on a direct current with a maximum voltage output of 15 kV (Fig. 4). Argon containing 10–30 vol % of methane was decomposed at temperatures of 10,000 K and contact times of $10^{-4}-10^{-5}$ s. Most of the methane was decomposed and 67–87% conversions to acetylene were obtained. The acetylene yield could be increased by using gas mixtures richer in methane[89–91)].

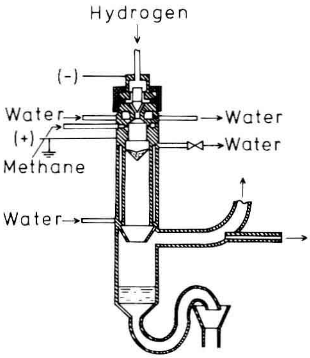

Fig. 4. Schematic of plasmatron system used for methane pyrolysis. (Redrawn from Kinetika i termodinam. khim. reaktsii v nizkotemperaturnoi plazme, Polak, L. (ed.). Moscow: Nauka 1965, by permission of Professor L. Polak, Institute of Petrochemical Synthesis of the Academy of Sciences of the U.S.S.R., Moscow)

Polak's calculations[80)] of the kinetics of conversion of methane to acetylene showed that acetylene concentration reached a maximum at a certain distance along the plasma jet (Fig. 5). Chilling (20–50 °C cm^{-1}) which was begun at a distance slightly less than the distance that corresponded to maximum concentration of C_2H_2, prevented a significant decrease of C_2H_2 in the part of the jet that followed the maximum. Heating of the jet over a short distance of its initial part (500 °C cm^{-1}) increased the extent of decomposition of methane, raised the maximum concentration of C_2H_2 and displaced the point at which the maximum concentration of C_2H_2 was reached toward the beginning of the jet. The optimum ratio for length to diameter of the reactor was 6.5–7.5; the number and diameter of the gas (methane) inlets were also significant[87)]. In a later work Andreev et al.[92)] reported similar variations in product concentrations along their reactor length. Methane pyrolysis in a hydrogen plasma jet with two stage methane addition showed that with proportions and quenching rates suitably adjusted for the second addition, ethylene and hydrogen, and not acetylene, were the major products[88)].

With natural gas[83–86)] containing 91% CH_4 by vol introduced into a hydrogen plasmatron at 4000–4500 K and with water chilling injected perpendicular to the gas flow the total decomposition was 94% and the conversion to C_2H_2 was as high as 76%. The composition by vol % of a typical gas mixture after the conversion was

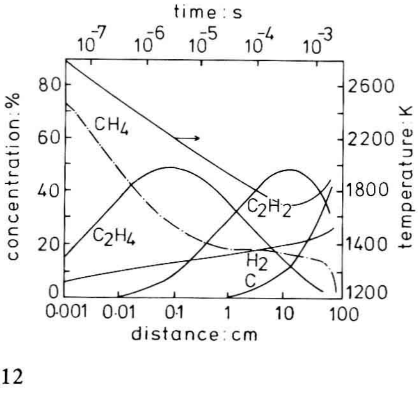

Fig. 5. Relations between the concentrations of methane pyrolysis products and the distance or time over which the reaction occurred. A temperature-time (distance) profile of the plasma jet is also shown. (Redrawn from Kinetika i termodinam. khim. reaktsii v nizkotemperaturnoi plazme, Polak, L. (ed.). Moscow: Nauka 1965, by permission of Professor L. Polak, Institute of Petrochemical Synthesis of the Academy of Sciences of the U.S.S.R., Moscow)